

COMPOSITION FOR THE PERMANENT DEFORMATION OF THE HAIR  
COMPRISING AT LEAST ONE FORMAMIDINESULPHINIC ACID  
DERIVATIVE

5           A subject-matter of the invention is a  
composition for the permanent deformation of the hair  
comprising at least one formamidinesulphinic acid  
derivative. The invention is also targeted at a process  
for the permanent deformation of the hair employing  
10 this composition.

          The technique for bringing about the  
permanent deformation of the hair consists, in a first  
step, in opening the disulphide bonds of the keratin  
(cystine) using a composition comprising a reducing  
15 agent (reduction stage) and then, preferably after  
having rinsed the hair, in reconstituting, in a second  
step, the said disulphide bonds by applying an  
oxidizing composition to the hair under tension  
(oxidation stage, also known as setting stage), so as  
20 to give the hair the desired shape. This technique  
makes it possible without distinction to either wave  
the hair or to straighten it.

          The compositions for carrying out the first  
stage of a perming operation are generally provided in  
25 the form of lotions, creams, gels or powders to be  
diluted in a liquid vehicle and comprise a reducing  
agent, preferably a thiol. Among the latter, those  
commonly used are cysteine and thioglycolic acid and

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its esters, in particular glyceryl monothioglycolate. Thioglycolic acid is particularly effective in reducing the disulphide bonds of keratin and can be regarded, at alkaline pH, in particular in the form of ammonium thioglycolate, as the reference compound in permanent waving. However, it exhibits a disadvantage of giving off an unpleasant smell. A fragrance which allows smells to be masked is generally used for the purpose of overcoming this disadvantage.

Cysteine has a much fainter smell than that of thioglycolic acid but the degree of curling obtained is much less and far from being satisfactory. Furthermore, cysteine requires the use of a highly alkaline pH.

Glyceryl monothioglycolate is also highly malodorous. In contrast, it is used at a pH close to neutrality but its performance is appreciably inferior to that of thioglycolic acid.

Various studies have been carried out for the purpose of overcoming the disadvantages of these reducing agents and, to this end, the use of novel reducing compounds has been proposed. Thus, Patent Application US 3 715 429 has disclosed a composition for the deformation of the hair comprising thiourea dioxide in combination with an activating agent.

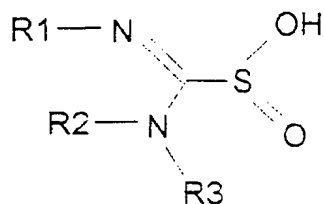
Nevertheless, the reducing compositions for permanent waves known to date are still not entirely

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satisfactory, given that damage to the hair fibre is excessively great.

The problem posed by the invention is to provide a reducing composition for the permanent deformation of the hair which is more effective than those which already exist, in particular in terms of degree, of liveliness or of quality of curling, while reducing the damage to the hair.

To solve this problem, the invention provides a reducing composition for the permanent deformation of the hair, characterized in that it comprises, as reducing agent, an N-substituted formamidinesulphinic acid derivative of following general formula (I):



(I)

in which:

(a) R1, R2 and R3, which are identical or different, represent a hydrogen atom, an amino, C1 to C8 amino-alkyl, imino, C1 to C8 aminoalkyl or guanidino group, a C1 to C8 linear or branched alkyl, C2 to C8 alkenyl or C7 to C20 aralkyl group, or an aromatic or nonaromatic C3 to C20 ring optionally comprising one or more heteroatom(s) chosen from halogens, nitrogen, oxygen or

sulphur; it being possible for all these substituents optionally to carry one or more hydroxyl, carboxyl, amino, amido, halogen, C1-C8 alkyl or C1-C8 alkoxy radicals, and

- 5 (b) at least one of the R1, R2 or R3 groups is an amino or C1 to C8 aminoalkyl group or is chosen from the alkyls, alkenyls, aralkyls, aryls or rings listed above in (a), these groups being, in addition, either directly substituted by at least one sulphonyl,
- 10 sulphonate, phosphonyl, phosphate, amino or C1 to C8 alkoxy radical or substituted by another C1 to C8 alkyl, C2 to C8 alkenyl or C7 to C20 aralkyl group, themselves substituted by a sulphonic acid, sulphonate, phosphoric acid, phosphate, amino or C1 to C8 alkoxy
- 15 radical;
- and the inorganic or organic salts of the said compounds of formula (I).

The invention also relates to the use of a compound of formula (I) as reducing agent, in

20 particular in a reducing composition intended for the permanent deformation or the straightening of the hair.

Yet another subject-matter of the invention relates to a process for the permanent deformation of the hair employing a reducing composition comprising at

25 least one compound of formula (I).

The R1, R2 and R3 groups chosen in order to obtain a compound of formula (I) as defined above are preferably selected from:

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- the hydrogen atom,
- linear or branched C1-C6 alkyls optionally substituted by at least one hydroxyl, carboxyl, amino, sulphonyl or phosphonyl radical,
- 5 - phenyls optionally substituted by at least one halogen atom or by a C1-C4 alkyl or C1-C4 alkoxy radical or alternatively hydroxyl,
- heterocycles, such as pyridine, dihydropyridine, tetrahydropyridine or quinoline, and
- 10 - the guanidino radical.

The compounds of formula (I) are generally prepared according to the procedures disclosed in the following references:

- E. Ya. Yarovenko et al., Zh. Org. Khim. (1970), 6
- 15 (5), 947-9;
- M.F. Kondrachova et al., Metody Poluch. Khim. Reaktivov Prep. (1969), No. 20, 56-7;
- D. De Filippo et al., J. Chem. Soc. Perkin Trans. II (1972), (11), 1500-2;
- 20 - J.J. Havel et al., Synth. Commun. (1974), 4 (6), 389-93; and
- Patent Applications SU 229521 and EP-A1 488749.

Mention may in particular be made, among the preferred compounds of general formula (I), of:

- 25 - imino(methylamino)methanesulphinic acid
- imino(propylamino)methanesulphinic acid
- (dimethylamino)iminomethanesulphinic acid
- (diethylamino)iminomethanesulphinic acid

- (ethylamino) (ethylimino) methanesulphinic  
acid

- (methylamino) (methylimino) methanesulphinic  
acid

5               - (ethylamino) (ethylimino) methanesulphinic  
acid

- (butylamino) (butylimino) methanesulphinic  
acid

- (phenylamino) (phenylimino) methanesulphinic  
10 acid

- (phenylmethylamino) (phenylmethylimino) -  
methanesulphinic acid

- (carboxymethylamino) iminomethanesulphinic  
acid

15               - (2-carboxyethylamino) iminomethanesulphinic  
acid

- (3-carboxypropylamino) iminomethanesulphinic  
acid

- (5-carboxypentylamino) iminomethanesulphinic  
20 acid

- (hydroxymethylamino) iminomethanesulphinic  
acid

- (2-aminoethylamino) iminomethanesulphinic  
acid

25               - imino(sulphonylmethylamino) methanesulphinic  
acid

- imino(2-sulphonylpropylamino) methane-  
sulphinic acid

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- imino(2-phosphonylmethylamino)methane-  
sulphinic acid
- imino(phenylamino)methanesulphinic acid
- imino(4-methylphenylamino)methanesulphinic  
5 acid
- imino(4-hydroxyphenylamino)methanesulphinic  
acid
- imino(4-methoxyphenylamino)methanesulphinic  
acid
- imino(2-chlorophenylamino)methanesulphinic  
10 acid
- imino(4-methyl-2-pyridylamino)methane-  
sulphinic acid
- imino(6-methyl-2-pyridylamino)methane-  
15 sulphinic acid
- imino(5-methyl-2-pyridylamino)methane-  
sulphinic acid
- imino(2-quinolylamino)methanesulphinic acid
- imino(3-quinolylamino)methanesulphinic acid
- (methylimino)-2-pyridylaminomethane-  
20 sulphinic acid
- (methylimino)[(3,4,5,6-tetrahydro-  
2-pyridyl)amino]methanesulphinic acid
- [(aminoiminomethyl)amino]iminomethane-  
25 sulphinic acid.

Preference is very particularly given to:

- (carboxymethylamino)iminomethanesulphinic acid, and
- imino(phenylamino)methanesulphinic acid.

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Mention may also be made, among the derivatives corresponding to the general formula (I) which are particularly well suited to the reducing compositions according to the invention, of those  
5 disclosed in Patent JP 93 239662, filed by Fuji.

The formamidinesulphinic acid derivative of formula (I) is advantageously formulated as an aqueous lotion, at a pH of between 2 and 11 and preferably between 7 and 10.

10 In accordance with the invention, the name "*formamidinesulphinic acid*" is equivalent to "amino-iminomethanesulphinic acid" or "thiourea dioxide".

The process in accordance with the invention for the permanent deformation of the hair comprises the  
15 application of a reducing composition comprising, as reducing agent, a compound of formula (I). The hair is shaped by using mechanical means well known to a person skilled in the art, such as curlers, the reducing composition being applied before and after the means  
20 for shaping the hair and a setting composition being applied after the reducing composition, with or without an intermediate or subsequent stage of rinsing or of application of intermediate composition.

According to the present invention, the  
25 permanent deformation of the hair preferably consists, in a first stage, in reducing the disulphide bonds of the keratin by application, for approximately 5 to 60 min, of a reducing composition as defined above and

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then, in a second stage, in reforming the said bonds by application of an oxidizing composition or optionally by allowing atmospheric oxygen to act.

Preferably, a reducing composition as defined  
5 above is applied to wet hair wound beforehand onto rollers having a diameter of 4 to 20 mm, it being possible for the composition optionally to be applied as the hair is wound on; the reducing composition is subsequently allowed to act for a time of 5 to 60  
10 minutes, preferably of 5 to 30 minutes, and then the hair is copiously rinsed; after which an oxidizing composition which makes it possible to reform the disulphide bonds of the keratin is applied to the wound hair for a exposure time of 2 to 10 minutes. After  
15 having removed the rollers, the hair is copiously rinsed.

The oxidizing composition is of the type commonly used and comprises, for example, as oxidizing agent, hydrogen peroxide, an alkaline bromate, a  
20 persalt, a polythionate or a mixture of alkaline bromate and of persalt. The concentration of hydrogen peroxide can vary from 1 to 20 volumes and preferably from 1 to 10, the concentration of alkaline bromate from 2 to 12% and that of persalt from 1 to 15% by  
25 weight with respect to the total weight of the oxidizing composition. The pH of the oxidizing composition is generally between 2 and 10. This

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oxidation can be carried out immediately or can be delayed.

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The deformation of the hair according to the invention can also consist of a process for  
5 straightening the hair, in which a reducing composition according to the invention is applied to the hair and then the hair is subjected to a mechanical deformation which makes it possible to set it in its new form by an operation in which the hair is smoothed with a wide-  
10 toothed comb, with the back of a comb or with the hand. After an exposure time of 5 to 60 minutes, in particular of 5 to 30 minutes, a fresh smoothing is then carried out, then the hair is carefully rinsed and an oxidizing or setting composition as defined above is  
15 applied, which composition is allowed to act for approximately 2 to 10 minutes, and then the hair is copiously rinsed.

In the perming compositions according to the invention, the reducing agent of general formula (I) is  
20 generally present at a concentration of between 0.05 and 20% and preferably between 0.1 and 8% by weight with respect to the total weight of the reducing composition.

The pH of the composition is preferably  
25 between 4 and 11 and more particularly between 6 and 10 and is obtained using an alkaline agent, such as, for example, aqueous ammonia, monoethanolamine, diethanolamine, triethanolamine, 1,3-propanediamine, an

alkali metal or ammonium carbonate or bicarbonate, an organic carbonate, such as guanidine carbonate, or an alkaline hydroxide, or using an acidifying agent, such as, for example, hydrochloric acid, acetic acid, lactic acid, oxalic acid or boric acid.

The reducing composition can also comprise, in combination, another known reducing agent, such as, for example, thioglycolic acid, glyceryl or glycol monothioglycolate, cysteamine and its C1-C4 acylated derivatives, such as N-acetylcysteamine or N-propionylcysteamine, cysteine, N-acetylcysteine, the N-mercaptoalkylamides of sugars, such as N-(2-mercaptoethyl)-gluconamide,  $\beta$ -mercaptopropionic acid and its derivatives, thiolactic acid and its esters, such as glyceryl monothiolactate, thiomalic acid, pantheteine, thioglycerol, sulphites or bisulphites of an alkali metal or alkaline earth metal, the N-(mercaptoalkyl)-o-hydroxyalkylamides disclosed in Patent Application EP 354 835 and the N-mono- or N,N-dialkylmercapto-4-butyramides disclosed in Patent Application EP 368 763, the aminomercaptoalkylamides disclosed in Patent Application EP 403 267 and the alkylamino-mercaptoalkylamides disclosed in Patent Application EP 432 000.

According to a preferred embodiment, the reducing composition also comprises a surface-active agent of nonionic, anionic, cationic or amphoteric type and mention may be made, among these, of alkyl

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sulphates, alkylbenzenesulphates, alkyl ether  
sulphates, alkylsulphonates, quaternary ammonium salts,  
alkyl betaines, oxyethylenated alkylphenols, fatty acid  
alkanolamides, oxyethylenated fatty acid esters and  
5 other nonionic surfactants of the hydroxypropyl ether  
type.

When the reducing composition comprises at  
least one surface-active agent, the latter is generally  
present at a maximum concentration of 30% by weight and  
10 preferably of between 0.5 and 10% by weight with  
respect to the total weight of the reducing  
composition.

With the aim of improving the cosmetic  
properties of the hair or alternatively of lessening or  
15 preventing their damage to them, the reducing  
composition can also comprise a treating agent of  
cationic, anionic, nonionic or amphoteric nature.

Mention may in particular be made, among the  
particularly preferred treating agents, of those  
20 disclosed in French Patents No. 2 598 613 and No.  
2 470 596. Use may also be made, as treating agents, of  
volatile or nonvolatile and linear or cyclic silicones  
and their mixtures, polydimethylsiloxanes, quaternized  
polyorganosiloxanes, such as those disclosed in French  
25 Patent Application No. 2 535 730, polyorganosiloxanes  
with aminoalkyl groups modified by alkoxycarbonylalkyl  
groups, such as those disclosed in US Patent No.  
4 749 732, polyorganosiloxanes, such as the

polydimethylsiloxane-polyoxyalkyl copolymer of the dimethicone copolyol type, a polydimethylsiloxane with stearoxy end groups (stearoxy dimethicone), a polydimethylsiloxane-dialkylammonium acetate copolymer  
5 or a polydimethylsiloxane-poly(alkyl betaine) copolymer which are disclosed in British Patent No. 2 197 352, polysiloxanes organomodified by mercapto or mercapto-alkyl groups such as those disclosed in French Patent No. 1 530 369 and in European Patent Application No.  
10 295 780, and silanes, such as stearoxytrimethylsilane.

The reducing composition can also comprise other treating ingredients, such as cationic polymers, such as those used in the compositions of French Patents Nos. 79.32078 (2 472 382) and 80.26421  
15 (2 495 931), or cationic polymers of the ionene type, such as those used in the compositions of Luxembourgian Patent No. 83 703, basic amino acids (such as lysine or arginine) or acidic amino acids (such as glutamic acid or aspartic acid), peptides and their derivatives,  
20 protein hydrolysates, waxes, swelling and penetrating agents or agents which make it possible to reinforce the effectiveness of the reducing agent, such as the SiO<sub>2</sub>/PDMS (polydimethylsiloxane) mixture, dimethylisorbitol, urea and its derivatives, pyrrolidone,  
25 N-alkylpyrrolidones, thiamorpholinone, or alkyl ethers of alkylene glycol or of dialkylene glycol, such as, for example, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, ethylene glycol

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monoethyl ether and diethylene glycol monoethyl ether, C3-C6 alkanediols, such as, for example, 1,2-propanediol and 1,2-butanediol, 2-imidazolidinone and other compounds, such as fatty alcohols, lanolin derivatives, 5 active ingredients, such as panthothenic acid, agents for combating hair loss, antidandruff agents, thickeners, suspending agents, sequestering agents, opacifying agents, colorants or sunscreen agents, as well as fragrances and preservatives.

10           The reducing composition according to the invention is provided essentially in the aqueous form, in particular in the form of a thickened or non-thickened lotion, of a cream or of a gel.

15           The reducing composition according to the invention can also be of the exothermic type, that is to say of the type which gives rise to a degree of warming when applied to the hair, which is pleasing to the person who is undergoing the first stage of the perming or hair straightening.

20           The reducing composition according to the invention can also comprise a solvent, such as, for example, ethanol, propanol or isopropanol, or glycerol, at a maximum concentration of 20% with respect to the total weight of the composition.

25           The vehicle of the compositions according to the invention is preferably water or an aqueous/ alcoholic solution of a lower alcohol, such as ethanol, isopropanol or butanol.

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When the compositions are intended for an operation for straightening the hair, the reducing composition is preferably in the form of a thickened cream, so as to keep the hair as straight as possible.

5 These creams are prepared in the form of "heavy" emulsions, for example based on glyceryl stearate, on glycol stearate, on self-emulsifiable waxes or fatty alcohols.

It is also possible to use liquids or gels  
10 comprising thickening agents, such as carboxyvinyl polymers or copolymers which "stick" the hair together and keep it in the smooth position during the exposure time.

The invention also relates to a kit, in  
15 particular for the permanent deformation of the hair, comprising, in a first compartment, as reducing composition, a composition according to the invention comprising a compound of formula (I) and, in a second compartment, an oxidizing composition.

20 The invention may be better understood with the help of the following nonlimiting example which constitutes a preferred embodiment of the compositions according to the invention.

## 25 Examples

A lotion 1 in accordance with the prior art, comprising formamidinesulphinic acid as reducing agent, and a lotion 2 in accordance with the present

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invention, comprising a derivative of formula I, namely N-phenylformamidinesulphinic acid, as reducing agent, are prepared. The compositions of these two lotions are shown in Table I below.

5

Table I

	Lotion 1	Lotion 2
Formamidinesulphinic acid	0.5 M	-
N-Phenylformamidine-sulphinic acid	-	0.5 M
Diethylenetriamine-pentaacetic acid, pentasodium salt, as an aqueous solution comprising 40% a.m.	0.2 g	0.2 g
Monoethanolamine	q.s. for pH 9	q.s. for pH 9
Water	q.s. for 100 g	q.s. for 100 g

The lotion 1 or 2 is applied to locks of natural European chestnut-brown hair. Curls are formed using curlers. The lotion is allowed to act on the wound hair for 15 minutes. The combination is dried with a hairdryer for 5 minutes. The hair is rinsed with water. A conventional setting composition based on hydrogen peroxide is applied. Rinsing is again carried out. The curlers are removed.

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It is observed that, with the lotion 1 in accordance with the prior art, the modification in the shape of the hair is slight, whereas the lotion 2 produces a much greater and more marked deformation in  
5 the shape of the hair.

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